

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE	
ATTORNEY DOCKET NO. 0492611-0482	
Applicants: Anish Goel, et al.	Art Unit: 1754
Application. No.: 10/675,140	Examiner: McCracken, Daniel.
Filed: September 30, 2003	Customer Number: 24280
<b>FULLERENIC STRUCTURES AND SUCH STRUCTURES TETHERED TO CARBON MATERIALS</b>	

### 132 DECLARATION

Jack B. Howard declares as follows:

1. I am a co-inventor of the subject matter of the above-identified patent application.
2. I am Professor Emeritus of Chemical Engineering at Massachusetts Institute of Technology (MIT) in Cambridge, Massachusetts.
3. My research has focused on combustion and the flame synthesis of carbon nanostructures including fullerenes, nanotubes, and fullerenic black or soot. For 40 years members of my research group and I at MIT studied the chemical kinetics and mechanisms of formation of carbon materials, including graphitic, diamond, diamond-like and, in the last 20 years, fullerenic carbon, in flames and other high-temperature systems. I have co-authored or authored over 100 peer-reviewed publications on these topics. Almost half of these publications are concerned with fullerenes, nanotubes and other fullerenic carbon nanostructures.
4. My co-inventors and I conceived of chemically attaching fullerenes to bulk carbon materials.
5. The present application describes how fullerenes are chemically bonded to a bulk carbon surface.
6. I have studied carefully the prior references of record along with the Donnet reference provided by the examiner during a recent telephone interview.
7. As to the teachings in the Japanese laid-open publication number 11-140342, I conclude that the reference does not establish the chemical bonding of fullerenes to carbon black as mentioned on page 1 of the present application. My conclusion has a strong scientific basis, summarized as follows.

Although the Japanese reference refers to "fullerenes to be bound to the surface of the carbon black" (4, [0011]), I can find no indication in the reference that "bound to the

surface” was meant to refer to chemical bonding. Furthermore, there is not to my knowledge any known basis for assuming that fullerenes bound to carbon black would involve chemical bonding. To the contrary, it would be assumed based on well known behavior experienced in fullerenes production, collection and separations operations that a reference to fullerenes bound to carbon surfaces would be referring to physical bonds or van der Waals interactions, not chemical bonds. As is now widely known and discussed in authoritative reference books for students and professionals (e.g., the Dresselhaus et al. book cited below), fullerenes are produced along with a particulate carbon by-product referred to with different names including, soot, fullerene black, fullerenic black, and solid carbon. This material is similar to carbon black except it is composed of curved-layer or fullerenic carbon instead of planar or graphitic carbon. Because of inherent strain in curved carbon layers, fullerenes are somewhat more strongly bound to fullerenic black than they would be to carbon black. However, even the bonding to fullerenic black is by relatively weak physical bonds, not chemical bonds which are much stronger. Evidence that the fullerenes are bound to fullerenic black with physical, not chemical, bonds can be seen from the wide use of solvent extraction or sublimation for separating the fullerenes from the fullerenic black on which they condense as the two are produced and recovered together (Dresselhaus et al., *Science of Fullerenes and Carbon Nanotubes*, Academic Press, 1996, Chapter 5, in particular Chapters 5.2 and 5.3). Extraction is a well known and widely practiced separation process. It is only used when the components being separated are physically mixed and interacting with physical forces, not chemical bonds, between them. Confirmation of this understanding is provided by Dresselhaus et al. (ibid., Chapter 5.2, p. 116), “Two distinct methods are employed to extract the fullerenes from the soot. In the most common method, the so-called solvent method, toluene or some other appropriate solvent is used to dissolve the fullerenes. ....The soot and other insolubles are therefore easily separated from this solution by filtration, or simply by decanting the solution. In a second, or “sublimation method”, the raw soot containing the fullerenes is heated in a quartz tube in He gas, or in vacuum ( $\sim 10^{-5}$  torr), to sublime the fullerenes, which then condense in a cooler section of the tube, leaving the soot and other nonvolatiles behind in the hotter section of the tube.” In this description, the use of a solvent “to dissolve the fullerenes” and the use of heating “to sublime the fullerenes” mean the fullerenes are only physically bound to the soot. If they were chemically bound, they would neither dissolve nor sublime, both of which processes are purely physical, involving the release of a molecule from a solid material by overcoming physical attractive forces. No chemical bond breaking is involved. Obviously, since the fullerenes are only physically bound to fullerene black, they will certainly be only physically bound to carbon black with which they interact even less strongly than with fullerenic black.

8. I have also carefully studied US Patent 6,358,375 to Schwob and a journal article by Donnet et al. entitled “Fullerenic Carbon in Carbon Black Furnaces” (Donnet, J.B., et al., *Carbon*, 2000, 38, 1865-1866) provided by the examiner as mentioned above and it is my opinion that these references do not disclose fullerenes chemically bonded to a bulk carbon surface. This opinion is based on well founded scientific information as explained below.

The Schwob patent effectively teaches that the fullerenes are physically, not chemically, bound to carbon black. The patent explicitly teaches that "the carbon black with the accumulated fullerenes may be taken from the process, and be subjected to further purification. The further purification may be carried out in accordance with a known method, for example by extraction (Dresselhaus et al., Science of Fullerenes and Carbon Nanotubes, Academic Press, 1996, Chapter 5, pp. 111, in particular Chapters 5.2 and 5.3)" (Schwob 4, 46-53)." The Schwob recommendation of extraction for the purification, i.e., the removal of fullerenes from the carbon black, means that Schwob understands the fullerenes to be physically bound, not chemically bonded, to the carbon black. The reasoning here is the same as that explained in detail above in point 7.

The Donnet paper presents electron micrograph images of carbon black particles and interprets them as (i) "showing the fullerene structure inside the particle" (Fig. 1) and (ii) "showing the fullerene structure on the surface of the particle" (Fig. 2). Donnet et al. cite this and other papers from their group as having (iii) "established beyond doubt that fullerene structures exist both in the bulk and on the surface of carbon black particles..." (p. 1885, col. 2, last sentence, continuing to p.1886). They also say (iv) "we could even identify C<sub>60</sub>....in the toluene extracts of the same carbon blacks" (p.1886, col. 1, lines 3-5). They further say (v) the fullerene structures they see are strikingly similar to those published by Howard and coll. (p.1886, col. 1, lines 6-8). My comments on each of the above points are given below using the same numbering system as that used above.

(i) The fullerene structures seen inside carbon black particles in Donnet's work and inside fullerene black or fullerene soot particles in the work of Howard et al. (e.g., refs. 4, 5 and 16 in the above Donnet paper) are indeed fullerene carbon, meaning they consist of curved layers, as distinct from flat or planar layers which are well known to be characteristic of graphitic carbon. However, the Donnet et al. paper and the cited papers of Howard et al. do not show any images of fullerene molecules inside the particles. Donnet et al. do not claim to see fullerene molecules in their figures. Instead they simply refer to the structures as fullerene.

The fullerene structures reported by Donnet et al. and the MIT group exhibit various shapes and sizes and different degrees or approaches to complete closure. Many of the structures are open or incompletely closed and for this reason they were referred to as shells in the first work reporting them (ref. 4 in the above Donnet paper). Whether any of these fullerene structures are stable fullerene molecules such as C<sub>60</sub> and C<sub>70</sub> is open to question. Whether such fullerene molecules could even be seen in electron microscope images was questionable at the time of Donnet's work and at the time of the MIT work cited by Donnet. According to S. Iijima, the discoverer of single-walled carbon nanotubes and widely regarded the world's preeminent electron microscopist of fullerene carbon materials, a small round object the size of a C<sub>60</sub> molecule he and Ajayan reported seeing in an electron microscope image could not be a C<sub>60</sub> molecule because C<sub>60</sub> would be too small to give a strong enough signal to form the observed image (Ajayan, P.M. and Iijima, S., Nature, 1992, 358, 23). Instead Iijima said the image must be that of a single-walled carbon nanotube viewed down its longitudinal axis. [Later work at MIT showed that C<sub>60</sub> fullerene can give an observable electron microscope image if the molecule is

held in the electron beam of the microscope long enough to give sufficient signal for imaging. Experience at MIT (Goel et al., Carbon, 2004, 42, 1907-1913) and elsewhere (Fuller, T. and Banhart, F., Chem. Phys. Lett., 1996, 254, 372-378) revealed that C<sub>60</sub> physically deposited (i.e., physically condensed or adsorbed) on a carbon surface moves or jumps out of the beam before sufficient signal could be captured. In the MIT work, C<sub>60</sub> is held in place by chemically bonding it to the surface of a carbon black particle (Goel et al., *ibid.*).

Workers familiar with carbon materials will understand that incompletely closed curved layers or shells will have reactive atoms in the edges of layers which will be found bonded with adjacent structures, and that regions of high curvature corresponding to radii of curvature smaller than the radius of C<sub>60</sub> fullerene (0.35 nm) will be highly strained, potentially unstable, and stabilized by contact with adjacent structures. Therefore the fullerenic structures seen inside particles can be assumed to be bonded to the adjacent structures with either chemical bonds involving edge atoms or relatively strong physical bonds involving regions of high curvature, i.e., radii of curvature less than that of C<sub>60</sub> fullerene. None of the observed structures described above are fullerene molecules chemically bonded to a carbon surface or bulk carbon material.

(ii) The fullerenic structures referred to in the Donnet paper, Fig. 2, as being on the surface have small radii of curvature similar to that of fullerene C<sub>60</sub> or C<sub>70</sub>, but the images do not indicate whether the structures seen are open or closed. In contrast, the work of Howard et al. (e.g., ref. 16 [Grieco et al., Carbon, 2000, 38, 597-614] cited by Donnet et al.) shows various apparently closed structures with radii of curvature similar not only to that of C<sub>60</sub> or C<sub>70</sub> but also to smaller and larger fullerenes, in the surface region of fullerenic soot particles. However, Grieco et al. did not actually know whether these structures are fullerene molecules and referred to them only as closed-shell structures. They pointed out that "...the presence of fullerene molecule-sized closed shells in the soot is consistent with fullerenes being present in the gas phase and reactively depositing on the growing soot particle..." and "...consistent with gas-phase fullerenes being consumed by reactions with the growing soot particles..." (p.613 of Grieco et al.), but they did not call them fullerenes. The reasons for such caution in the identification of what appears to be closed-shells in the size range of fullerene molecules are that these structures could be: (1) single-walled nanotubes as suggested by Iijima, (2) only incompletely closed shells whose lack of closure cannot be discerned in the microscope images, or (3) closed carbon cages without the perfect isolated-pentagon structure of stable fullerenes.

(iii) The existence of fullerenic structures in the bulk or on the surface of carbon black particles does not disclose fullerenes chemically bonded in the bulk or on the surface of carbon black particles because (1) the fullerenic structures may not be fullerene molecules (as mentioned above, Donnet et al. do not claim the structures seen in their figures are actually fullerenes) and (2) as explained above in discussions of the Japanese and Schwob patents, there is no precedent or reason for believing that fullerenes found with carbon black particles after the two were produced together in a high temperature process are chemically bound to the carbon black.

(iv) The observed presence of  $C_{60}$  in toluene extracts of the same carbon black means that the  $C_{60}$  was not chemically bound to the carbon black; it must have been only physically bound else it would not have been extractable with toluene.

(v) As mentioned in (ii) above, Howard and coll. did report the presence of fullerene molecule-sized closed shells in the soot but they never referred to them as fullerenes. The reasons for such caution in the identification of the closed shells are given in (ii) above. Therefore, even though the fullerenic structures seen by Donnet et al. might be strikingly similar to those seen by Howard and coll., this does not mean that Donnet et al. were observing fullerenes chemically bound to bulk carbon because (1) there is no basis or reason to assume they were observing fullerenes, and (2) even if the observed fullerenic structures were fullerenes there would be no basis or reason for assuming them to be chemically bound.

9. I have carefully reviewed the Remo patent number 5,132,105 and Taylor article (Taylor, R. and Walton, D.R.M., "The Chemistry of Fullerenes", Nature, 1993, 363, 685-693) and conclude that while carbon to carbon chemical bonds are disclosed, these references do not teach or suggest the chemical bonding of a fullerene to a surface of bulk carbon material. This conclusion has a firm scientific basis, summarized as follows:

Remo teaches how to grow structures of tetrahedral carbon, which refers to diamond or diamond-like carbon, using fullerenes as feedstock. According to Remo, the fullerenes unwind and break up (Remo 3, lines 21 and 22) and the broken fullerenes are converted to diamond and/or diamond-like particles (Remo 7, line 57-59). Thus Remo teaches the consumption of fullerenic carbon to form tetrahedral carbon (i.e., diamond or diamond-like) structures, and hence Remo teaches a fullerene molecule bonded to the tetrahedral structures growing out of a newly formed bond with the fullerene molecule (Remo 3, 1-7). However, Remo does not disclose a fullerene molecule bonding to bulk carbon. Although fullerene molecules are shown in the patent (Figs. 3 and 4) the fullerenes are not shown bonded to bulk carbon. Figure 4 shows bonding between the fullerene cage and tetrahedral carbon atoms, but the atoms are in small molecular sized clusters, not bulk carbon. Thus the picture presented by Remo is a  $C_{60}$  molecule reacting with gaseous molecules, e.g., carbon compounds (Remo 1, 52-53) or carbon containing gases (Remo, Abstract, 3<sup>rd</sup> line) from a flame or plasma fed with  $C_2H_2$  (Remo 3, 55) or methane ( $CH_4$ ) (Remo 4, 36; 5, 40 and 6, 23), to form "new tetrahedral structures growing out of the newly formed bond" (Remo 3, 4-6). Furthermore the foregoing is only an intermediate or passing step along the way to the final diamond or diamond-like material taught by Remo. The final material does not contain or is not bonded to an intact  $C_{60}$  molecule. Instead, the carbon atoms originally in the  $C_{60}$  molecule are incorporated in the diamond material (Remo 3, 21-22; 7, 57-59). Therefore, the Remo patent does not teach the production of a stable final product involving a  $C_{60}$  molecule bonded to diamond, diamond-like, or any other bulk carbon material or surface, nor does Remo claim that a stable chemical bond could be formed between a  $C_{60}$  molecule and diamond, diamond-like or any other bulk carbon material or surface.

The Taylor article is concerned with fullerenes and their derivatives, meaning fullerenes bonded to molecular functional groups including other fullerenes as in polymerization. Taylor does not teach fullerenes bonded to bulk material or the surface of bulk material. Chemical bonding between a fullerene and bulk carbon material or the surface of bulk carbon material would be very different from chemical bonding of the fullerene with a molecule of the bulk carbon material. Such a molecule would be a radical species whose reactivity in forming chemical bonds would be exceedingly high relative to that of the bulk carbon material or its surface.

10. I further state that all the statements of my own knowledge are true and that all statements made on information and belief are believed to be true. I have been warned that willful false statements and the like are punishable by fine or imprisonment, or both (18 U.S.C. 1001) and may jeopardize the validity of the application or any patent issuing thereon.

Respectively submitted,

Date: July 10, 2007

Jack B. Howard  
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